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(71) Applicant:

Asahi Kasei Kogyo Kabushiki Kaisha
Osaka-shi, Osaka 530-8205 (JP)

(72) Inventors:

- IOKA, Takaaki
Shizuoka-ken 416-0939 (JP)
- TANABE, Tsuneaki
Shizuoka-ken 417-0855 (JP)

(74) Representative:

Strehl Schübel-Hopf & Partner
Maximilianstrasse 54
80538 München (DE)

**(54) ALKOXYSLANE/ORGANIC POLYMER COMPOSITION FOR THIN INSULATING FILM
PRODUCTION AND USE THEREOF**

(57) Disclosed is an alkoxy silane/organic polymer composition for use in producing an insulating thin film, comprising (A) a specific alkoxy silane; (B) a specific organic polymer; and (C) a solvent for alkoxy silane (A) and organic polymer (B), wherein solvent (C) comprises at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents. Also disclosed are a silica-organic polymer composite thin film which is produced by a process comprising: forming a thin film of the composition of the present invention; subjecting the thin film to a hydrolysis and dehydration-condensation reaction with respect to the alkoxy silane thereof, to thereby cause the alkoxy silane to be gelled in the thin film; and removing the solvent remaining in the thin film by drying, and a porous silica thin film which is obtained by removing the organic polymer from the silica-organic polymer composite thin film. Both of the silica-organic polymer composite thin film and the porous silica thin film have advantages not only in that these thin films have a low dielectric constant suitable for insulating layers for a multilevel interconnect for a semiconductor device, but also in that these thin films can be produced by a method which can be easily performed in

the current process for producing a semiconductor device.

Description**BACKGROUND OF THE INVENTION****5 Field of the invention**

[0001] The present invention relates to an alkoxy silane/organic polymer composition for use in producing an insulating thin film. More particularly, the present invention is concerned with an alkoxy silane/organic polymer composition for use in producing an insulating thin film, comprising (A) a specific alkoxy silane; (B) a specific organic polymer; and (C) a solvent for alkoxy silane (A) and organic polymer (B), wherein the solvent (C) comprises at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents. In a current process for producing a semiconductor device, a silicon oxide insulating layer is produced by a method comprising dissolving a silicon oxide precursor in an appropriate solvent to thereby obtain a solution of the silicon oxide precursor, forming a coating of the obtained solution on a substrate by spin coating technique or the like, and calcining the coating at an appropriate temperature. When the composition of the present invention is used as a material for an insulating layer in the production of a multilayer circuit structure for a semiconductor device, an insulating layer having a low dielectric constant can be produced by a method which can be easily performed in the current process for producing a semiconductor device. The present invention is also concerned with a multilayer circuit structure for a semiconductor device, which comprises a plurality of insulating layers and circuits formed on the insulating layers, wherein at least one layer of the insulating layers is obtained using the above-mentioned composition. Further, the present invention is concerned with a semiconductor device comprising the above-mentioned multilayer circuit structure.

Background Art

25 [0002] Conventionally, as a material for an insulating layer for a multilayer circuit structure for a semiconductor device, such as an LSI, silica (having a dielectric constant of from 4.0 to 4.5) or the like has generally been used. In recent years, the density of the circuit of a semiconductor device (such as an LSI) has become higher and higher, and, hence, the distance between mutually adjacent conducting lines in the circuit has become extremely small. As a consequence of this, the mutually adjacent conducting lines having insulators therebetween have inadvertently come to function as a condenser. This has posed a problem that, when the dielectric constant of the insulator is high, the electrostatic capacity of the condenser inadvertently formed by the mutually adjacent conducting lines and the insulators present therebetween becomes high, so that the transmission of the electric signals through each of the mutually adjacent conducting lines is markedly delayed. In order to solve this problem, with respect to a material for an insulating layer for a multilayer circuit structure, studies have been made to develop a material having a much lower dielectric constant.

30 [0003] It is known that, among conventional materials, polytetrafluoroethylene has a lowest dielectric constant, which is approximately 1.9. However, in general, fluororesins have a problem in that fluororesins have not only poor adhesion to a substrate and a circuit but also poor heat resistances. Further, in recent years, the dielectric constant of an insulating layer is required to be less than 1.9.

35 [0004] On the other hand, attempts have been made in which the dielectric constant of a conventional material is decreased by rendering the material porous, thereby providing a porous material which is a composite comprised of the conventional material and air (having a dielectric constant of 1.0).

40 [0005] A silica aerogel (which is a type of porous silica) is a representative example of such porous materials. However, production of a silica aerogel requires supercritical drying. Therefore, production of a silica aerogel requires not only a long time, but also extremely complicated steps of operations using a specially designed apparatus, so that it is practically impossible to introduce a step for producing a silica aerogel insulating layer into the current process for producing a semiconductor device.

45 [0006] U.S. Patent No. 5,472,913 discloses a method for producing a porous silica by a special technique requiring no supercritical drying. However, this method still requires extremely complicated steps of operations, so that it is difficult to introduce a step in which a porous silica insulating layer is produced by this method into the current process for producing a semiconductor device.

50 [0007] Journal of Macromolecular Science-Chemistry, A27, 13-14 p.1603 (1990) discloses a method for producing a porous silica, which comprises subjecting an alkoxy silane to a hydrolysis and dehydration-condensation reaction in the presence of a specific organic polymer so as to cause a gelation of the alkoxy silane, thereby obtaining a homogeneous organic-inorganic composite comprised of the organic polymer and silica, and heating the obtained composite for calcination so that the organic polymer in the composite can be thermally decomposed and removed, thereby obtaining a porous silica. However, in this method, the calcination for completely decomposing and removing the

organic polymer is required to be conducted in an atmosphere of air at a temperature as high as 600 °C or more, so that it is impossible to introduce a step in which a porous silica insulating layer is produced by this method into the current process for producing a semiconductor device.

[0008] Further, as described below, methods for producing a porous thin film or the like, which are similar to the above-mentioned method disclosed in Journal of Macromolecular Science-Chemistry, are disclosed in Unexamined Japanese Patent Application Laid-Open Specification Nos. 8-245278 and 7-100389 and WO97/06896.

[0009] Unexamined Japanese Patent Application Laid-Open Specification No. 8-245278 discloses a method for producing a porous ceramic thin film, which comprises coating a substrate with an alcohol solution of a metal alkoxide, which solution contains polyethylene glycol added thereto, and calcining the resultant coating.

[0010] Unexamined Japanese Patent Application Laid-Open Specification No. 7-100389 discloses a method for producing a carrier for a catalyst for use in petroleum refining, which comprises subjecting a metal alkoxide to a hydrolysis and dehydration-condensation reaction in the presence of an organic polymer, and calcining the resultant product.

[0011] WO97/06896 discloses a method for producing a porous metal oxide film, which comprises dissolving a metal alkoxide, an acid and an organic polymer in a mixed solvent of a first solvent and water to thereby obtain a coating solution, coating the obtained solution onto a glass substrate to form a gel film on the substrate, drying the gel film, immersing the dried gel film in a second solvent to extract and remove the organic polymer from the gel film, and calcining the gel film to thereby obtain a porous metal oxide film.

[0012] It is noted that, in each of the methods disclosed in Unexamined Japanese Patent Application Laid-Open Specification Nos. 8-245278 and 7-100389 and WO97/06896, an alcohol is used as a solvent for each of the metal alkoxide and the organic polymer. For the reason as described below, the use of an alcohol as a solvent disadvantageously causes a lowering of the void ratio of an obtained porous material, thereby making it impossible to obtain such a porous insulating thin film having a low dielectric constant as can be suitably used in a multilayer circuit structure for a semiconductor device.

[0013] As is apparent from the above, such an insulating thin film having a low dielectric constant as can be suitably used in a multilayer circuit structure for a semiconductor device has conventionally been unable to be produced by a method which can be easily performed in the current process for producing a semiconductor device.

SUMMARY OF THE INVENTION

[0014] In this situation, the present inventors have made extensive and intensive studies with a view toward developing an insulating thin film for use in a multilayer circuit structure for a semiconductor device, wherein the insulating thin film not only has a low dielectric constant, but also can be produced by a method which can be easily performed in the current process for producing a semiconductor device. As a result, it has unexpectedly been found that the above objective can be attained by using an alkoxysilane/ organic polymer composition comprising (A) a specific alkoxysilane; (B) a specific organic polymer; and (C) a solvent for alkoxysilane (A) and organic polymer (B), wherein the solvent (C) comprises at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents. More specifically, it has unexpectedly been found that an insulating thin film produced from the above alkoxysilane/organic polymer composition not only has a low dielectric constant which is suitable for an insulating layer for a multi-layer circuit structure for a semiconductor device, but also can be produced by a method which can be easily performed in the current process for producing a semi-conductor device, wherein the insulating thin film is either a silica-organic polymer composite thin film (produced by forming a thin film from the above alkoxysilane/organic polymer composition and then subjecting the thin film to heat treatment) or a porous silica thin film (obtained by removing the organic polymer from the silica-organic polymer composite thin film). The present invention has been completed, based on the above novel finding.

[0015] Therefore, it is a primary object of the present invention to provide a composition for use in producing an insulating layer for a multilayer circuit structure for a semiconductor device, wherein the insulating layer not only has a low dielectric constant, but also can be produced by a method which can be easily performed in the current process for producing a semiconductor device.

[0016] It is another object of the present invention to provide a composite insulating thin film which can be produced from the above-mentioned composition, and a porous silica thin film which can be obtained from the above composite insulating thin film, as well as the uses of these thin films.

[0017] The foregoing and other objects, features and advantages of the present invention will be apparent to those skilled in the art from the following detailed description and appending claims.

DETAILED DESCRIPTION OF THE INVENTION

[0018] In one aspect of the present invention, there is provided an alkoxysilane/organic polymer composition for use in producing an insulating thin film, comprising:

(A) at least one alkoxy silane selected from the group consisting of (1) tetraalkoxysilanes, (2) trialkoxysilanes, (3) dialkoxy silanes, (4) monoalkoxysilanes and (5) trialkoxysilane dimers, respectively, represented by the following formulae (1), (2), (3), (4) and (5):

5	Si(OR)_4	(1).
10	$\text{R}^1\text{Si(OR)}_3$	(2).
	$\text{R}^1\text{R}^2\text{Si(OR)}_2$	(3).
15	$\text{R}^1\text{R}^2\text{R}^3\text{SiOR}$ and	(4).
20	$(\text{RO})_3\text{Si-R}^4\text{-Si(OR)}_3$	(5).

wherein each R independently represents a straight chain or branched alkyl group having 1 to 6 carbon atoms, each of R^1 , R^2 and R^3 independently represents a hydrogen atom or a monovalent hydrocarbon group having 1 to 6 carbon atoms, and R^4 represents a divalent hydrocarbon group having 1 to 6 carbon atoms, and wherein, when the alkoxy silane (A) is at least one first alkoxy silane selected from the group consisting of the alkoxy silanes (3) and (4), the first alkoxy silane is used in combination with at least one second alkoxy silane selected from the group consisting of the alkoxy silanes (1), (2) and (5);

(B) at least one organic polymer having a main chain mainly comprising at least one polymer chain selected from the group consisting of an aliphatic polyether chain having ether group-containing recurring units having 2 to 12 carbon atoms, an aliphatic polyester chain having ester group-containing recurring units having 2 to 12 carbon atoms, an aliphatic polycarbonate chain having carbonate group-containing recurring units having 2 to 12 carbon atoms and an aliphatic polyanhydride chain having anhydride group-containing recurring units having 2 to 12 carbon atoms; and

(C) a solvent for the alkoxy silane (A) and the organic polymer (B), wherein the solvent (C) comprises at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents.

[0019] For easy understanding of the present invention, the essential features and various embodiments of the present invention are enumerated below.

1. An alkoxy silane/organic polymer composition for use in producing an insulating thin film, comprising:

(A) at least one alkoxy silane selected from the group consisting of (1) tetraalkoxysilanes, (2) trialkoxysilanes, (3) dialkoxy silanes, (4) monoalkoxysilanes and (5) trialkoxysilane dimers, respectively, represented by the following formulae (1), (2), (3), (4) and (5):

40	Si(OR)_4	(1).
45	$\text{R}^1\text{Si(OR)}_3$	(2).
	$\text{R}^1\text{R}^2\text{Si(OR)}_2$	(3).
50	$\text{R}^1\text{R}^2\text{R}^3\text{SiOR}$ and	(4).
55	$(\text{RO})_3\text{Si-R}^4\text{-Si(OR)}_3$	(5).

wherein each R independently represents a straight chain or branched alkyl group having 1 to 6 carbon atoms, each of R^1 , R^2 and R^3 independently represents a hydrogen atom or a monovalent hydrocarbon group having 1 to 6 carbon atoms, and R^4 represents a divalent hydrocarbon group having 1 to 6 carbon atoms, and wherein, when the alkoxy silane (A) is at least one first alkoxy silane selected from the group consisting of the alkoxy silanes (3) and (4), the first alkoxy silane is used in combination with at least one second alkoxy silane selected from the group consisting of the alkoxy silanes (1), (2) and (5);

(B) at least one organic polymer having a main chain mainly comprising at least one polymer chain selected from the group consisting of an aliphatic polyether chain having ether group-containing recurring units having 2 to 12 carbon atoms, an aliphatic polyester chain having ester group-containing recurring units having 2 to 12 carbon atoms, an aliphatic polycarbonate chain having carbonate group-containing recurring units having 2 to 12 carbon atoms and an aliphatic polyanhydride chain having anhydride group-containing recurring units having 2 to 12 carbon atoms; and

carbon atoms, an aliphatic polycarbonate chain having carbonate group-containing recurring units having 2 to 12 carbon atoms and an aliphatic polyanhydride chain having anhydride group-containing recurring units having 2 to 12 carbon atoms; and

5 (C) a solvent for the alkoxy silane (A) and the organic polymer (B), wherein the solvent (C) comprises at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents.

2. The composition according to item 1 above, wherein the alkoxy silane (A) is a mixture of at least one tetraalkoxy silane (1) and at least one alkoxy silane selected from the group consisting of the alkoxy silanes (2) to (5).

10 3. The composition according to item 1 above, wherein the alkoxy silane (A) is at least one trialkoxy silane (2), or a mixture of at least one trialkoxy silane (2) and at least one alkoxy silane selected from the group consisting of the alkoxy silanes (1) and (3) to (5).

15 4. The composition according to any one of items 1 to 3 above, wherein the solvent (C) further comprises at least one alcohol.

20 5. The composition according to any one of items 1 to 4 above, which further comprises (D) at least one acid capable of functioning as a catalyst for promoting a hydrolysis and dehydration-condensation reaction of the alkoxy silane (A).

25 6. The composition according to any one of items 1 to 5 above, wherein the organic polymer (B) is an aliphatic polyether comprising a polyalkylene glycol having C_2 to C_{12} ether group-containing recurring units and having a number average molecular weight of from 200 to 1,000,000.

7. The composition according to any one of items 1 to 6 above, wherein the organic polymer (B) is present in an amount of from 0.1 to 10 in terms of a weight ratio relative to the amount of a product obtained by subjecting the entire amount of the alkoxy silane (A) to a hydrolysis and dehydration-condensation reaction.

30 8. A silica-organic polymer composite thin film, which is produced by a process comprising:

forming a thin film of the composition of any one of items 1 to 7 above;
subjecting the thin film to a hydrolysis and dehydration-condensation reaction with respect to the alkoxy silane (A) thereof, to thereby cause the alkoxy silane (A) to be gelled in the thin film; and
removing the solvent (C) remaining in the thin film by drying.

35 9. The silica-organic polymer composite thin film according to item 8 above, which has a thickness of from 0.1 to 100 μ m.

40 10. The silica-organic polymer composite thin film according to item 8 or 9 above, which is transparent to visible rays having a wavelength of from 0.4 to 0.7 μ m.

45 11. A multilayer circuit structure comprising a plurality of insulating layers and circuits formed on the insulating layers, wherein at least one layer of the insulating layers comprises the silica-organic polymer composite thin film of any one of items 8 to 10 above.

12. A semiconductor device comprising the multilayer circuit structure of item 11 above.

50 13. A porous silica thin film which is obtained by removing the organic polymer from the silica-organic polymer composite thin film of any one of items 8 to 10 above.

14. The porous silica thin film according to item 13 above, which has an average pore diameter of from 1 to 500 nm.

55 15. The porous silica thin film according to item 13 or 14 above, wherein the removal of the organic polymer from the silica-organic polymer composite thin film is performed by calcining the composite thin film at a temperature of not higher than 450 °C.

16. The porous silica thin film according to any one of items 13 to 15 above, which has a surface thereof treated

with a silylating agent.

17. A multilayer circuit structure comprising a plurality of insulating layers and circuits formed on the insulating layers, wherein at least one layer of the insulating layers comprises the porous silica thin film of any one of items 13 to 16 above.

18. A semiconductor device comprising the multilayer circuit structure of item 17 above.

[0020] Hereinbelow, the present invention will be described in detail.

[0021] At least one alkoxy silane which is used as component (A) of the alkoxy silane/organic polymer composition of the present invention is selected from the group consisting of (1) tetraalkoxysilanes, (2) trialkoxysilanes, (3) dialkoxysilanes, (4) monoalkoxysilanes and (5) trialkoxysilane dimers, respectively, represented by the following formulae (1) to (5):



25 wherein each R independently represents a straight chain or branched alkyl group having 1 to 6 carbon atoms, each of R¹, R² and R³ independently represents a hydrogen atom or a monovalent hydrocarbon group having 1 to 6 carbon atoms, and R⁴ represents a divalent hydrocarbon group having 1 to 6 carbon atoms. Examples of alkyl groups which can be suitably used as R in formulae (1), (2), (3), (4) and (5) above include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group and a t-butyl group. Examples of monovalent hydrocarbon groups which can be suitably used as R¹, R² and R³ in formulae (2), (3) and (4) above include a methyl group and a phenyl group. Further, examples of divalent hydrocarbon groups which can be suitably used as R⁴ in formula (5) above include a methylene group, an ethylene group, an isopropylidene group and a phenylene group.

[0022] It is preferred that the alkoxy silane (A) comprises at least one alkoxy silane selected from the group consisting of alkoxy silanes (1), (2) and (5), to which, if desired, at least one alkoxy silane selected from the group consisting of alkoxy silanes (3) and (4) is added.

[0023] It is especially preferred that the alkoxy silane (A) is:

- 1) a mixture of at least one of the above-mentioned alkoxy silane (1) and at least one alkoxy silane selected from the group consisting of the above-mentioned alkoxy silanes (2) to (5);
- 2) at least one of the above-mentioned trialkoxysilane (2); or
- 3) a mixture of at least one of the above-mentioned trialkoxysilane (2) and at least one alkoxy silane selected from the group consisting of the above-mentioned alkoxy silanes (1) and (3) to (5).

[0024] When the alkoxy silane (A) is at least one first alkoxy silane selected from the group consisting of the alkoxy silanes (3) and (4), the first alkoxy silane is used in combination with at least one second alkoxy silane selected from the group consisting of alkoxy silanes (1), (2) and (5).

[0025] When the alkoxy silane (A) is only at least one alkoxy silane selected from the group consisting of the alkoxy silanes (3) and (4), the alkoxy silane (A) cannot be gelled by a method in which a thin film obtained from the composition of the present invention for use in producing an insulating thin film is subjected to a hydrolysis and dehydration-condensation reaction with respect to the alkoxy silane (A) thereof. Therefore, in such a case, any of the silica-organic polymer composite thin film and porous silica thin film of the present invention described below cannot be obtained.

[0026] In the above-mentioned preferred form 1) of the alkoxy silane (A), when the amount of the at least one alkoxy silane selected from the group consisting of the above-mentioned alkoxy silanes (2) to (5) is reduced and the amount of the above-mentioned tetraalkoxysilane (1) is increased, the crosslinking density of the product obtained by the hydrolysis and dehydration-condensation reaction of the above-mentioned alkoxy silane (A) is increased, so that the mechanical strength of the silica-organic polymer composite thin film and porous silica thin film of the present invention described below is improved.

[0027] On the other hand, in the above-mentioned preferred form 1) of the alkoxy silane (A), when the amount of the

above-mentioned tetraalkoxysilane (1) is reduced and the amount of the at least one alkoxy silane selected from the group consisting of the above-mentioned alkoxy silanes (2) to (5) is increased, the crosslinking density of the product obtained by the hydrolysis and dehydration-condensation reaction of the above-mentioned alkoxy silane (A) is lowered, so that the product has an improved cracking resistance. Further, when the hydrocarbon groups are directly bonded to the silicon atoms, the hygroscopicity of the above-mentioned reaction product is extremely reduced by the influence of the hydrocarbon groups.

[0028] At least a part of the alkoxy silane (A), which is at least one alkoxy silane selected from the group consisting of the above-mentioned alkoxy silanes (1) to (5), is optionally in the form of an oligomer, and at least a part of the alkoxy silane (A), which is at least one alkoxy silane selected from the group consisting of the above-mentioned alkoxy silanes (1) to (3) and (5), is optionally in a partially hydrolyzed form. Further, metal alkoxides which can be condensed with the above-mentioned alkoxy silanes (1) to (5), may be optionally added to the above-mentioned alkoxy silanes (1) to (5). Examples of such optional metal alkoxides include C₁-C₆ alkoxides of aluminum, titanium, zirconium, baron, magnesium, germanium, zinc, tin, niobium, lead, strontium, lithium and barium. Among these, C₁-C₆ alkoxides of aluminum, titanium and zirconium are preferred. The amount of the optional metal alkoxide is preferably 30 % by weight or less, based on the weight of the alkoxy silane (A).

[0029] Specific examples of alkoxy silanes which can be used as the above-mentioned alkoxy silanes (1) to (5) include tetramethoxysilane, tetraethoxysilane, tetra(n-propoxy)silane, tetra(i-propoxy)silane, tetra(n-butoxy)silane, tetra(t-butoxy)silane, trimethoxysilane, triethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, phenyldimethoxysilane, phenyldiethoxysilane, methylldimethoxysilane, methylldiethoxysilane, phenylmethyldimethoxysilane, phenylmethyldiethoxysilane, trimethylmethoxysilane, trimethylethoxysilane, triphenylmethoxysilane, triphenylethoxysilane, phenyldimethylmethoxysilane, phenyldimethylethoxysilane, diphenylmethylmethoxysilane, diphenylmethylethoxysilane, dimethylmethoxysilane, dimethylethoxysilane, diphenylmethoxysilane, diphenylethoxysilane, bis(trimethoxysilyl)methane, bis(triethoxysilyl)methane, 1,2-bis(trimethoxysilyl)ethane, 1,2-bis(triethoxysilyl)ethane, 1,4-bis(trimethoxysilyl)benzene and 1,4-bis (triethoxysilyl)benzene. Among these, especially preferred are tetramethoxysilane, tetraethoxysilane, trimethoxysilane, triethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, trimethylmethoxysilane and trimethylethoxysilane.

[0030] As is apparent from the below-mentioned specific examples of organic polymers usable as component (B), the organic polymer (B) of the alkoxy silane-organic polymer composition of the present invention comprises at least one organic polymer having a main chain mainly comprising at least one polymer chain selected from the group consisting of an aliphatic polyether chain having ether group-containing recurring units having 2 to 12 carbon atoms, an aliphatic polyester chain having ester group-containing recurring units having 2 to 12 carbon atoms, an aliphatic polycarbonate chain having carbonate group-containing recurring units having 2 to 12 carbon atoms and an aliphatic polyanhydride chain having anhydride group-containing recurring units having 2 to 12 carbon atoms.

[0031] The organic polymer (B) may be a single polymer or a mixture of a plurality of polymers. As long as the effect of the present invention is not adversely affected, the organic polymer (B) may optionally comprise a polymer chain having recurring units other than the above-mentioned recurring units. Further, the main chain of the organic polymer (B) may optionally have a functional group at terminals thereof. Usually, in a polyether, a polyester, a polycarbonate and a polyanhydride, the terminal groups are comprised of a hydroxyl group and/or a carboxyl group. However, the terminal groups of the main chain of the organic polymer (B) are not particularly limited to hydroxyl and carboxyl groups. As long as the effect of the present invention is not adversely affected, the terminal groups of the main chain of the organic polymer (B) may optionally be modified with other functional groups.

[0032] Examples of aliphatic polyethers having ether group-containing recurring units having 2 to 12 carbon atoms include polyalkylene glycols, such as polyethylene glycol, polypropylene glycol, polytrimethylene glycol, polytetramethylene glycol, polypentamethylene glycol, polyhexamethylene glycol, palydioxolane, polydioxepane and the like.

[0033] Examples of aliphatic polyesters having ester group-containing recurring units having 2 to 12 carbon atoms include polycondensation products of a hydroxycarboxylic acid and ring-opening polymerization reaction products of a lactone, such as polyglycolide, polycaprolactone, polycaprolactonetriol, polypivalolactone and the like; and polycondensation products of a dicarboxylic acid with an alkylene glycol, and ring-opening copolymerization products of an epoxide with an acid anhydride, such as polyethylene oxalate, polyethylene succinate, polyethylene adipate, polyethylene sebuate, polyethylene sebacate, polypropylene adipate, polyoxydiethylene malonate, polyoxydiethylene adipate and the like.

[0034] Examples of aliphatic polycarbonates having carbonate group-containing recurring units having 2 to 12 carbon atoms include polycondensation reaction products of carbonic acid and alkylene glycols, such as polyethylene carbonate, polypropylene carbonate, polytrimethylene carbonate, polytetramethylene carbonate, polypentamethylene carbonate, polyhexamethylene carbonate and the like.

[0035] Examples of aliphatic polyanhydrides having anhydride group-containing recurring units having 2 to 12 carbon atoms include polycondensation reaction products of dicarboxylic acids, such as polymalonyl oxide, polyadipoyl

oxide, polypimeloyl oxide, polysuberoyl oxide, polyazelaoyl oxide, polysebacoyl oxide and the like.

[0036] Of these, especially preferred are polyethylene glycol, polypropylene glycol, polycaprolactone, polycaprolactonetriol, polyethylene carbonate, polypentamethylene carbonate, polyhexamethylene carbonate, polyacipoyl oxide, polyazelaoyl oxide and polysebacoyl oxide.

5 [0037] The term "alkylene glycol" means a dihydric alcohol obtained by substituting an alkane having two, or more carbon atoms with two hydroxyl groups so that two hydrogen atoms bonded to different carbon atoms in the alkane are replaced by the hydroxyl groups. The term "dicarboxylic acid" means an organic acid having two carboxyl groups, such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid or the like.

10 [0038] When either aliphatic polymers other than the above-mentioned aliphatic polymers or aromatic polymers are used as organic polymer (B), problems arise in that the homogeneity of the silica-organic polymer composite thin film becomes poor and the required calcination temperature becomes high, thus rendering it difficult to produce any of the silica-organic polymer composite thin film and porous silica thin film of the present invention in the current process for producing a semiconductor device. However, for the purpose of adjusting the viscosity of the composition or improving 15 the coating properties of the composition, other optional polymers may be used in addition to organic polymer (B) defined in the present invention, as long as the desired effects of the present invention are not impaired.

20 [0039] The amount of the organic polymer (B) in the composition of the present invention varies depending on the physical properties desired for the silica-organic polymer composite thin film or the porous silica thin film. Generally, the amount of the organic polymer (B) is 10^{-2} to 100, preferably 10^{-1} to 10, more preferably 0.5 to 5, in terms of a weight ratio relative to the amount of a product obtained by subjecting the entire amount of the alkoxy silane (A) to a hydrolysis and dehydration-condensation reaction. When the above-defined weight ratio of the organic polymer (B) is less than 10^{-2} , problems arise in that a large-thickness coating of the composition cannot be obtained; that a good silica-organic polymer composite thin film having a satisfactory crack resistance cannot be obtained, and that a porous silica thin film having a satisfactory void ratio cannot be obtained. On the other hand, when the above-defined weight ratio of the 25 organic polymer (B) is larger than 100, problems arise in that any of the silica-organic polymer composite thin film and the porous silica thin film cannot have a satisfactory mechanical strength.

30 [0040] It is preferred that the organic polymer (B) has a number average molecular weight of from 200 to 1,000,000. It should be noted that the pore size of the porous silica thin film of the present invention is very small and has only a small dependency on the molecular weight of the organic polymer (B). This is a great difference between the present 35 invention and the conventional technique, and such difference is one of the reasons why the composite thin film and porous silica thin film of the present invention are especially excellent as insulating layers for a multilayer circuit structure for a semiconductor device.

40 [0041] In the alkoxy silane/organic polymer composition of the present invention, it is required that the solvent (C) for the alkoxy silane (A) and the organic polymer (B) comprise at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents. If such a solvent is not used, a gelation of the alkoxy silane (A) by the hydrolysis and dehydration-condensation reaction of the alkoxy silane (A) does not proceed efficiently, leading to a problem that, when the organic polymer (B) is removed from the silica-organic polymer composite thin film, the silica-organic polymer composite thin film shrinks, thereby making it impossible to obtain a porous silica thin film having a high void ratio and hence a low dielectric constant. This is the reason why a porous film having a high void ratio cannot be obtained by the techniques disclosed in the above-mentioned Unexamined Japanese Patent Application Laid-Open Specification Nos. 8-245278 and 7-100389 and WO97/06296.

45 [0042] The solvent (C) used in the present invention, i.e., at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents exhibits the effect to suppress an aggregation of the dispersed molecular chains of the organic polymer (B) in the silica-organic polymer composite film, thereby suppressing the growth of the polymer phase toward large particles. Generally, the interaction between silica and the organic polymer (B) used in the present invention is not strong. Therefore, if at least one organic 50 solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents is not used as the solvent (C), a problem arises that, during the course of the gelation of the alkoxy silane (A) in the production of the silica-organic polymer composite thin film, an aggregation of the molecular chains of the organic polymer (B) occurs, thereby forming large particles of the organic polymer (B) in the obtained silica-organic polymer composite thin film. If a porous silica thin film is produced from a silica-organic polymer composite thin film containing such large particles of the organic polymer (B), the removal of the organic polymer (B) causes the formation of large pores in the porous silica thin film, wherein the large pores are likely to adversely affect the multilayer circuit structure used as a semiconductor device.

55 [0043] With respect to the solvent (C), it is preferred that the amount of at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents in the solvent (C) is 1% by weight or more, based on the total weight of the solvent (C). If the amount of the above-mentioned at least one organic solvent is less than 1% by weight, based on the total weight of the solvent (C), an aggregation of

the molecular chains of the organic polymer (B) occurs, thereby forming large particles of the organic polymer (B) in the silica-organic polymer composite thin film, so that a problem tends to arise that a porous silica thin film having a small pore size and a high void ratio cannot be obtained.

[0044] Examples of amide linkage-containing solvents usable in the present invention include amides, such as formamide, N-methylformamide, N-ethylformamide, N,N-dimethylformamide, N,N-diethylformamide, N-methylacetamide, N-ethylacetamide, N,N-dimethylacetamide; N,N-diethylacetamide, N-methylpyrrolidone, N-formylmorpholine, N-acetyl-morpholine, N-formylpiperidine, N-acetylpirperidine, N-formylpyrrolidine, N-acetylpyrrolidine, N,N'-diformylpiperadine, N,N'-diacetylpirperadine and the like, and ureas, such as tetramethylurea, N,N'-dimethylimidazolidinone and the like.

10 Examples of ester linkage-containing solvents usable in the present invention include ethyl formate, methyl acetate, ethyl acetate, ethyl lactate, ethylene glycol monomethyl ether acetate, ethylene glycol diacetate, propylene glycol monomethyl ether acetate, diethyl carbonate, ethylene carbonate, propylene carbonate and the like. Of these, particularly preferred are N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, tetramethylurea, N,N'-dimethylimidazolidinone, ethylene glycol monomethyl ether acetate, ethylene glycol diacetate and propylene glycol monomethyl ether acetate.

15 [0045] One solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents may be used alone as the solvent (C). However, when either a mixed solvent of at least two different organic solvents selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents or a mixed solvent of at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents and at least one organic solvent other than the amide linkage-containing and ester linkage-containing organic solvents is used as the solvent (C), advantages can be obtained in that the viscosity of the composition and the evaporation rate of the solvent (C) can be easily controlled. Preferred examples of other organic solvents which can be employed in combination with at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents include alcohols, such as C₁-C₄ monohydric alcohols, C₁-C₄ dihydric alcohols, glycerol and the like; ethers, such as tetrahydrofuran, diethyl ether, di(n-propyl) ether, diisopropyl ether, diglyme, 1,4-dioxane, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, propylene glycol monomethyl ether, propylene glycol dimethyl ether and the like; ketones, such as acetone, methyl ethyl ketone, methyl propyl ketone, methyl (n-butyl) ketone, methyl isobutyl ketone, methyl amyl ketone, cyclopentanone, cyclohexanone and the like; nitriles, such as acetonitrile, propionitrile, n-butyronitrile, isobutyronitrile and the like; dimethyl sulfoxide, dimethyl sulfoxide, sulfolane and the like. Of these, particularly preferred are those solvents having a hydroxyl group, such as C₁-C₄ monohydric alcohols, C₁-C₄ dihydric alcohols, glycerol, ethylene glycol monomethyl ether and propylene glycol monomethyl ether. The reason why the use of such solvents having a hydroxyl group is preferred is because the use of such a solvent in the composition of the present invention improves the film forming properties of the composition, rendering it easy to form a thin film having a uniform film thickness.

30 [0046] It is preferred that the amount of the solvent (C) in the composition of the present invention is 0.05 % by weight or more, based on the weight of the composition. If the amount of the solvent (C) is less than 0.05 % by weight, based on the weight of the composition, a gelation of the alkoxy silane (A) by the hydrolysis and dehydration-condensation reaction thereof tends not to proceed efficiently, thereby rendering it difficult to produce not only a practically employable silica-organic polymer composite thin film but also a practically employable porous silica thin film.

35 [0047] The composition of the present invention may contain a substance which is capable of functioning as a catalyst for promoting the hydrolysis and dehydration-condensation reaction of the alkoxy silane (A). Examples of such substances which are capable of functioning as a catalyst include acids, such as hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, formic acid, acetic acid, oxalic acid, malonic acid, maleic acid, toluenesulfonic acid and the like; and bases, such as an aqueous ammonia solution, potassium hydroxide, sodium hydroxide, triethylamine, triethyl-anolamine, pyridine, piperidine, choline and the like. However, if a base is used as a catalyst, the pore size of the porous silica thin film tends to become too large. Therefore, the use of an acid is preferred. Acids and bases may be used individually or in combination. Further, if desired, the composition may be stepwise treated using an acid and a base. Herein, the term "stepwise treated" means a mode in which, for example, the composition is treated first with an acid and then with a base. Alternatively, the acid and the base may also be used in the reverse order. In those cases, two different types of catalysts are added to the composition.

40 [0048] When a catalyst is employed, the amount of the catalyst is 1 mole or less, preferably 10⁻¹ mole or less, per mole of the alkoxy silane (A). When the amount of the catalyst is more than 1 mole, per mole of the alkoxy silane (A), the catalyst tends to form a deposit, thereby rendering it difficult to obtain a homogeneous porous silica thin film.

45 [0049] Water is required for the hydrolysis of the alkoxy silane (A) in the present invention. The manner of supply of water is not specifically limited but can be made in any desired manner. For example, when a catalyst is employed, water may be added to the catalyst in advance. When a catalyst is added in an aqueous solution form, the water in the aqueous solution may be used for the hydrolysis of the alkoxy silane (A). Further, when the hydrolysis of alkoxy silane (A) is performed in an atmosphere containing a relatively large amount of steam and the amount of the steam is suffi-

cient to effect the hydrolysis, it is unnecessary to supply water. The amount of water suitable for the hydrolysis of the alkoxy silane (A) is 10^4 moles or less, preferably 10 moles or less, per mole of the silicon atoms contained in the alkoxy silane (A). Then the amount of water used is more than 10^4 moles, per mole of the silicon atoms contained in the alkoxy silane (A), the homogeneity of the silica-organic polymer composite thin film tends to become low.

5 [0050] If desired, various additives, such as a photocatalyst generator for imparting a photosensitivity, an agent for improving the adhesion to a substrate, and a stabilizer for a long-term storage, may be added to the composition of the present invention in such an amount as will not impair the effects of the present invention.

[0051] The silica-organic polymer composite thin film can be produced by a process comprising:

10 forming a thin film of the composition obtained by the above-mentioned manner; subjecting the thin film to a hydrolysis and dehydration-condensation reaction with respect to the alkoxy silane (A) thereof, to thereby cause the alkoxy silane (A) to be gelled in the thin film; and removing the solvent (C) remaining in the thin film by drying.

15 [0052] In the present invention, the term "silica" means both SiO_2 and a compound having a structure wherein a hydrocarbon group and a hydrogen atom are bonded to silicon atoms, specifically a structure represented by the following formula:



20 wherein R' represents a $\text{C}_1\text{-C}_6$ hydrocarbon group, $0 \leq x < 2$, $0 \leq y < 2$, $0 \leq (x + y) < 2$, and $1 < z \leq 2$.

[0053] The formation of a thin film is performed by coating a substrate with the composition of the present invention. As a method for forming a thin film, any conventional method, such as casting, immersing, spin coating and the like, can be employed. However, the spin coating method is suitable when the production of the insulating layer is intended in a current process for producing a multilayer circuit structure for a semiconductor device. The thickness of the thin film can be controlled within the range of from $0.1 \mu\text{m}$ to $100 \mu\text{m}$ by varying the viscosity of the composition and the revolution rate of the spin coater. When the thickness of the thin film is larger than $100 \mu\text{m}$, the thin film tends to suffer cracking. Generally, when the insulating layer is used in a multilayer circuit structure for a semiconductor device, the suitable thickness of the insulating layer is $0.5 \mu\text{m}$ to $5 \mu\text{m}$.

30 [0054] Examples of substrates include substrates comprised of a single element substance semiconductor, such as silicon or germanium, and substrates comprised of a compound semiconductor, such as gallium-arsenic or indium-antimony. These semiconductor substrates may be used in a form having formed thereon a thin film of a substance other than the substance used as a material for the substrate. Examples of substances for such a thin film formed on a semiconductor substrate include metals, such as aluminum, titanium, chromium, nickel, copper, silver, tantalum, tungsten, osmium, platinum, gold and the like; inorganic compounds, such as silicon dioxide, fluorinated glass, phosphate glass, boratephosphate glass, borosilicate glass, polycrystalline silicon, alumina, titania, zirconia, silicon nitride, titanium nitride, tantalum nitride, boron nitride, hydrogen silsesquioxane; and organic polymers, such as methyl silsesquioxane, amorphous carbon, fluorinated amorphous carbon and polyimide.

35 [0055] Prior to the formation of a thin film of the composition on a substrate, the surface of the substrate may be treated with an agent for improving the adhesion to the thin film. As examples of agents for improving the adhesion to the thin film, there can be mentioned substances used as a so-called silane coupling agent or chelate compounds of aluminum. Especially preferred examples of agents for improving the adhesion include 3-aminopropyltrimethoxysilane, 3-aminopropyltrithoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, vinyltrichlorosilane, vinyltrithoxysilane, 3-chloropropyltrimethoxysilane, 3-chloropropylmethyldichlorosilane, 3-chloropropylmethyldimethoxysilane, 3-chloropropylmethyldiethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, hexamethyldisilazane, (ethyl acetoacetato)aluminum diisopropylate, tris(ethyl acetoacetato)aluminium, bis(ethyl acetoacetato)aluminum monoacetylacetone, tris(acetylacetone)aluminum and the like. If desired, when the agent for improving an adhesion to the thin film is applied onto a substrate, other additives may be added to the agent, and the agent may be diluted with a solvent. The treatment of the surface of the substrate with the agent for improving an adhesion to the thin film is conducted by a known method.

40 [0056] When alkoxy silane (A) in the thin film which is obtained by the above-mentioned method is gelled by a hydrolysis and dehydration-condensation reaction, a reaction product having a three dimensional network structure similar to the structure of silicon dioxide is obtained.

45 [0057] There is no particular limitation with respect to the temperature for the hydrolysis and dehydration-condensation reaction of alkoxy silane (A) (hereinbelow, this temperature is simply referred to as "reaction temperature"). However, the reaction temperature is usually 0 to 180°C , preferably 30 to 150°C . When the reaction temperature is

lower than 0 °C, the reaction rate becomes small, so that the time required for the satisfactory gelation of the alkoxy silane (A) becomes disadvantageously long. On the other hand, when the reaction temperature is higher than 180 °C, formation of large voids tends to occur, so that the homogeneity of the below-mentioned silica-organic composite thin film is lowered. The time for the hydrolysis and dehydration-condensation reaction of alkoxy silane (A) varies depending on the temperature of the heat treatment, the amount of the catalyst and the like. However, usually, the reaction is completed within several minutes to several days.

[0058] In general, the gelation of the alkoxy silane (A) occurs simultaneously with the evaporation of at least a part of the solvent (C). However, by using a solvent having an appropriate boiling point and, if desired, an appropriate type of a catalyst in an appropriate amount, it is possible to control the rate of the gelation of the alkoxy silane (A) and the rate of the evaporation of the solvent (C).

[0059] In many cases, when the solvent (C) is appropriately selected so that at least a part of the solvent (C) remains in the thin film until the gelation of the alkoxy silane (A) satisfactorily proceeds, favorable results can be obtained. When the solvent (C) remains in the thin film at the point in time of completion of the gelation of the alkoxy silane (A), the thin film is subsequently subjected to drying so as to remove the solvent (C) remaining in the thin film.

[0060] Needless to say, the temperature for drying varies depending on the type of the solvent (C). Usually, the temperature for drying is 30 to 250 °C. It is also effective to perform the drying under a reduced pressure. It is also preferred that the drying is performed while gradually elevating the temperature so as to avoid the occurrence of voids and obtain a homogeneous silica-organic polymer composite thin film.

[0061] By the above-mentioned method, a silica-organic polymer composite thin film can be obtained. The organic polymer (B) is dispersed in the obtained composite thin film almost in the form of molecular chains without suffering aggregation. When the above-mentioned dispersion of the molecular chains of the organic polymer (B) in the composite thin film is achieved, the composite thin film is transparent to visible rays having a wavelength of 0.4 to 0.7 μm.

[0062] The thus obtained silica-organic polymer thin film has a low dielectric constant, as compared to the silicon dioxide obtained using only alkoxy silane(s). Further, the thickness of the silica-organic polymer thin film can be rendered satisfactorily large. Therefore, the silica-organic polymer thin film as such can be used as an insulating layer for a multilayer circuit structure for a semiconductor device. However, in order to obtain an insulating layer for a multilayer circuit structure for a semiconductor device, which has a further lower dielectric constant, it is preferred that this composite thin film is converted to a porous silica thin film. The composite thin film can be converted to a porous silica thin film by removing the organic polymer (B) from the composite thin film. If the gelation of the alkoxy silane (A) has satisfactorily proceeded, when the organic polymer (B) is removed from the composite thin film, the spaces in the composite thin film, which had been occupied by the molecular chains of the organic polymer (B), are not collapsed but left as pores in the porous silica thin film. As a result, a porous silica thin film having a high void ratio and hence a low dielectric constant can be obtained.

[0063] Examples of methods for removing the organic polymer (B) include calcination by heating, plasma treatment, solvent extraction and the like. Among these methods, calcination by heating is preferred since calcination by heating can be easily performed in the current process for producing a semiconductor device. When the organic polymer (B) is removed by calcination, the calcination temperature varies depending on the type of the organic polymer (B) used. The calcination temperature is usually 300 to 500 °C, preferably 350 to 450 °C. When the calcination temperature is higher than 500 °C, the pores of the resultant porous silica thin film are likely to be collapsed, so that the thickness of the thin film is extremely decreased and the dielectric constant of the thin film becomes disadvantageously high. On the other hand, when the calcination temperature is lower than 300 °C, the organic polymer (B) is not satisfactorily decomposed, so that some organic substances derived from the organic polymer (B) may remain in the resultant porous silica thin film as impurities, and, hence, it becomes difficult to obtain a porous silica thin film having a low dielectric constant.

[0064] The calcination is conducted for 1 minute to 24 hours. When the calcination time is shorter than 1 minute, the organic polymer (B) is not satisfactorily decomposed, so that some organic substances derived from the organic polymer (B) may remain in the resultant porous silica thin film as impurities, and, hence, it becomes difficult to obtain a porous silica thin film having a low dielectric constant. In general, thermal decomposition of the organic polymer (B) is completed within 24 hours. Therefore, a long-time calcination for more than 24 hours is useless.

[0065] The calcination can be conducted in an atmosphere of an inert gas, such as argon, helium and the like, or in an oxidizing atmosphere, such as an atmosphere of an oxygen-containing gas (for example, air and the like). In general, when the calcination is conducted in an oxidizing atmosphere, the calcination temperature tends to be lowered and the calcination time tends to become short. When the calcination is conducted in an atmosphere of a gas containing ammonia or hydrogen, nitridation or hydrogenation of the porous silica thin film occurs due to the reaction of the silanol groups remaining in the product obtained by the hydrolysis and dehydration-condensation reaction of alkoxy silane (A), so that the hygroscopicity of the resultant porous silica thin film can be advantageously lowered.

[0066] The silica-organic polymer composite thin film and porous silica thin film, each of which is obtained from the composition of the present invention, can be fabricated into a desired shape by a conventional method used in a current process for producing a semiconductor device.

[0066] Surface treatment of the obtained porous silica thin film with a silylating agent is effective for lowering the hygroscopicity of the porous silica thin film and improving the adhesion of the porous silica thin film to other substances. Examples of silylating agents include alkoxy silanes, such as trimethylmethoxysilane, trimethylmethoxysilane, dimethylimidethoxysilane, dimethyldiethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, dimethylethoxysilane, methylidioethoxysilane, dimethylvinylmethoxysilane, dimethylvinylethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, phenyltrimethoxysilane and phenyltriethoxysilane; chlorosilanes, such as trimethylchlorosilane, dimethylchlorosilane, methyltrichlorosilane, methyl dichlorosilane, dimethylchlorosilane, methylvinylchlorosilane, methylchlorodisilane, triphenylchlorosilane, methyl diphenylchlorosilane and diphenylchlorosilane; and silazanes, such as hexamethyldisilazane, N,N'-bis(trimethylsilyl)urea, N-(trimethylsilyl)acetamide, dimethyl(trimethylsilyl)amine, diethyl(trimethylsilyl)amine and trimethylsilylimidazole. Examples of methods for the silylation include application of the silylating agent by coating, immersing in the silylating agent or a solution thereof, exposure to the vapor of the silylating agent, and the like.

[0067] In a current process for producing a semiconductor device, a silicon oxide insulating layer for a multilayer circuit structure for a semiconductor device is produced by a method comprising dissolving a silicon oxide precursor in an appropriate solvent to thereby obtain a solution of the silicon oxide precursor, forming a coating of the obtained solution on a substrate by spin coating technique or the like, and calcining the coating at an appropriate temperature. When the alkoxy silane/organic polymer composition of the present invention (which comprises (A) a specific alkoxy silane; (B) a specific organic polymer; and (C) a solvent for alkoxy silane (A) and organic polymer (B), wherein solvent (C) comprises at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents) is used in place of the above-mentioned solution of the silicon oxide precursor and subjected to a treatment similar to the above-mentioned current process for producing an insulating thin film, an insulating layer of a multilayer circuit structure for a semiconductor device, which has a low dielectric constant, can be easily produced.

[0068] When the composition of the present invention is used, a silica-organic polymer composite thin film having a low dielectric constant or a porous silica thin film having micropores in a high void ratio and hence having a low dielectric constant can be obtained by a method which can be easily performed in the conventional process for producing a semiconductor device without any special equipment. Therefore, the composition of the present invention is extremely useful as a material for an insulating layer for a multilayer circuit structure, which has a low dielectric constant, especially as a material for an insulating layer for a multilayer circuit structure for an LSI.

BEST MODE FOR CARRYING OUT THE INVENTION

[0069] Hereinbelow, the present invention will be described in more detail with reference to the following Examples and Comparative Examples, which should not be construed as limiting the scope of the present invention.

[0070] In the following Examples and Comparative Examples, various properties of a silica-organic polymer composite thin film and of a porous silica thin film were evaluated by the following methods.

(1) Measurement of the surface area (N₂ BET):

Measurement was performed by means of Nitrogen Adsorption Isotherm Surface Area Measurement Apparatus (manufactured and sold by Shimadzu Corporation, Japan).

(2) Measurement of the film thickness:

Measurement was performed by means of DEKTAK-II A Model surface roughness measurement apparatus (manufactured and sold by Sloan Technology Corporation, U.S.A.).

(3) Measurement of the dielectric constant:

Measurement was performed by means of HP4280 Model C-V measurement apparatus (manufactured and sold by Hewlett-Packard Company, U.S.A.).

(4) Evaluation of the transparency:

Evaluation was made by the following method. A silica-organic polymer composite thin film is cut into a slice having a thickness of 1 mm. The slice was placed on a plate carrying a black character having a size of 3 mm x 3 mm so that the character is covered by the slice. The character is then visually observed through the slice. If the character is legible through the slice, the slice is evaluated as being transparent.

[0071] The number average molecular weight (M_n) of an organic polymer used herein was measured by gel permeation chromatography (GPC) using tetrahydrofuran as an eluent and using a calibration curve obtained with respect to standard monodispersed polystyrene systems.

[0072] The following abbreviations are used in Tables 1 to 7 showing the data of Examples and Comparative Examples.

TEOS: tetraethoxysilane,
 MTES: methyltriethoxysilane,
 TMOS: tetramethoxysilane,
 MTMS: methyltrimethoxysilane,
 5 PEG: polyethylene glycol,
 PCL: polycaprolactone,
 PC: poly(pentamethylene-hexamethylene carbonate),
 PVVE: polyvinyl ethyl ether,
 PVdF: polyvinylidene fluoride,
 10 NMP: N-methylpyrrolidone,
 DMF: N,N-dimethylformamide,
 EA: ethyl acetate,
 EtOH: ethanol, and
 MeOH: methanol

15

Example 1

[0073] 1.2 g of tetraethoxysilane and 0.34 g of polyethylene glycol (number average molecular weight: 20,000) were dissolved in 2.0 g of N-methylpyrrolidone. Then, added thereto were 0.30 g of water and 0.15 g of 0.1 N nitric acid, and
 20 the resultant solution was stirred for 2 hours at room temperature. This solution was cast onto a polytetrafluoroethylene watch-glass and allowed to stand for 1 hour at 120 °C to thereby cause the tetraethoxysilane to be gelled. The resultant gel was dried in vacuum at 180 °C, to thereby obtain a silica-organic polymer composite thin film. The obtained composite thin film was transparent.

25

Examples 2 to 14

[0074] Substantially the same procedure as in Example 1 was repeated, except that the types of the alkoxy silane, the organic polymer and the solvent were varied. The types and amounts of alkoxy silanes, organic polymers and solvents which were employed and the obtained results are shown in Table 1. The term "weight of gel" indicated in Table
 30 1 means the weight of a hydrolysis and dehydration-condensation reaction product of an alkoxy silane employed, as determined by calculation, based on the assumption that the entire amount of the alkoxy silane undergoes a hydrolysis and dehydration-condensation reaction.

[0075] All of the obtained silica-organic polymer thin films were transparent.

35

Table 1

Example No.	Alkoxy silane	Amount of alkoxy silane (g)	Weight of gel (g)	Polymer	Molecular weight of polymer	Amount of polymer (g)	Solvent	Appearance of gel
1	TEOS	1.2	0.34	PEG	20000	0.34	NMP	Transparent
2	TEOS	1.2	0.34	PEG	20000	0.68	NMP	Transparent
3	MTES	0.9	0.34	PEG	20000	0.34	DMF	Transparent
4	MTES	0.9	0.34	PEG	600	0.51	NMP	Transparent
5	MTMS	0.7	0.34	PEG	20000	0.34	NMP	Transparent
6	MTMS	0.7	0.34	PEG	1000	0.68	EA	Transparent
7	TMOS+MTMS (1/1)	0.8	0.34	PEG	2000	0.51	EA	Transparent

Table 1 (continued)

Example No.	Alkoxysilane	Amount of alkoxysilane (g)	Weight of gel (g)	Polymer	Molecular weight of polymer	Amount of polymer (g)	Solvent	Appearance of gel
8	TEOS	1.2	0.34	PCL	600	0.34	DMF	Transparent
9	MTMS	0.7	0.34	PCL	600	0.34	DMF	Transparent
10	MTMS	0.7	0.34	PC	20000	0.34	NMP	Transparent
11	TEOS	1.2	0.34	PEG	20000	0.68	NMP+EtOH (2/8)	Transparent
12	MTES	0.9	0.34	PEG	20000	0.85	NMP+EtOH (2/8)	Transparent
13	MTMS	0.7	0.34	PEG	600	1.05	DMF+EG (5/5)	Transparent
14	MTMS	0.7	0.34	PEG	20000	0.34	NMP+MeOH (3/7)	Transparent

Comparative Examples 1 to 4

[0076] Substantially the same procedure as in Example 1 was repeated, except that Polyvinyl ethyl ether (PVEE) and polyvinylidene fluoride (PVdF) were used as organic polymers. The results are shown in Table 2. A transparent and homogeneous gel could not be obtained in Comparative Examples 1 to 4.

Table 2

Compara. Ex. No.	Alkoxysilane	Amount of alkoxysilane (g)	Weight of gel (g)	Polymer	Molecular weight of polymer	Amount of polymer (g)	Solvent	Gelation
1	TEOS	1.2	0.34	PVEE	3800	0.34	NMP	Homogeneous gelation did not occur.
2	TEOS	1.2	0.34	PVdF	71000	0.34	DMF	Opaque gel was formed.
3	MTMS	0.7	0.34	PVdF	71000	0.34	NMP	Opaque gel was formed.
4	MTMS	0.7	0.34	PVdF	71000	0.34	EA	Opaque gel was formed.

Examples 15 to 26

[0077] 0.17 g of one polymer selected from the group consisting of polyethylene glycol (number average molecular weight: 20,000), polycaprolactone (number average molecular weight: 600) and polypentamethylhexamethylene carbonate (number average molecular weight: 2,000) was dissolved in 1.5 g of one solvent selected from the group con-

sisting of N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP), ethyl acetate and a mixed solvent (weight ratio: 6/4) of tetrahydrofuran (THF) and DMF. Then, added thereto were 0.60 g of tetraethoxysilane (corresponding to 0.17 g in terms of SiO_2) and 0.15 g of 0.1 N hydrochloric acid, and the resultant solution was stirred for 1 hour at room temperature. When 0.5 g of 0.1 N aqueous ammonia solution was added to this solution, tetraethoxysilane gelled rapidly and the whole of the solution became a jelly-like product.

[0078] As shown in Table 3, all of the obtained jelly-like products were colorless and transparent.

Table 3

Example No.	Polymer	Appearance of gel			
		DMF	NMP	Ethyl acetate	THF+DMF (6/4)
15-18	PEG	T	T	T	T
19-22	PCL	T	T	T	T
23-26	PC	T	T	T	T

T: Transparent,
O: Opaque

Comparative Examples 5 to 7

[0079] Substantially the same procedures as in Examples 15 to 26 were repeated, except that acetonitrile was used as the solvent. As shown in Table 4, all of the obtained jelly-like products were white opaque.

Table 4

Compara. Ex. No.	Polymer	Appearance of gel
Acetonitrile		
5	PEG	O
6	PCL	O
7	PC	O

T: Transparent,
O: Opaque

Example 27

[0080] 0.43 g of ETHYL SILICATE 40 (manufactured and sold by Colcoat Kabushiki Kaisha, Japan) and 0.17 g of polypropylene glycol (number average molecular weight: 4,000) were dissolved in a mixed solvent of 1.2 g of dimethylformamide and 0.8 g of ethanol. Then, added thereto was 0.2 g of 0.1 N aqueous ammonia solution. The resultant solution was cast onto a petri dish so as to form a thin film thereon. Then, the petri dish was sealedly covered and allowed to stand overnight at room temperature to thereby cause ETHYL SILICATE 40 to be gelled. Subsequently, the temperature of the atmosphere surrounding the thin film was gradually elevated from 60 °C to 120 °C and then the pressure of the atmosphere surrounding the thin film was reduced to vacuum while maintaining the temperature at 120 °C, thereby drying the thin film, thus obtaining a transparent silica-organic polymer composite thin film having a thickness of 1.3 mm. The obtained composite thin film was calcined for 2 hours at 450 °C in air, thereby removing the organic polymer to obtain a porous silica thin film. The specific surface area of the obtained porous silica thin film was measured by nitrogen adsorption isotherm method, and was found to be 990 m²/g. This value indicates that the pore diameter of the obtained porous silica thin film is small.

Comparative Example 8

[0081] 0.43 g of ETHYL SILICATE 40 (manufactured and sold by Colcoat Kabushiki Kaisha, Japan) and 0.17 g of polystyrene were dissolved in 2.0 g of methyl ethyl ketone. Further, added thereto was 0.2 g of 0.1 N aqueous ammonia solution. The resultant solution was cast onto a petri dish to thereby form a thin film. Then, the petri dish was sealedly

covered and allowed to stand overnight at room temperature to thereby cause ETHYL SILICATE 40 to be gelled. Subsequently, the temperature of the atmosphere surrounding the thin film was gradually elevated from 60 to 120 °C and then the pressure of the atmosphere surrounding the thin film was reduced to vacuum while maintaining the temperature at 120 °C, thereby drying the thin film, thus obtaining an opaque silica-organic polymer composite thin film. The obtained composite thin film was calcined for 2 hours at 450 °C in air, thereby removing the organic polymer to obtain a porous silica thin film. The specific surface area of the obtained porous silica thin film was measured using 0.13 g of the porous silica thin film, and found to be as small as 1 m²/g or less. This indicates that the pore diameter of the obtained porous silica thin film is large.

10 Example 28

[0082] 1.2 g of tetraethoxysilane (TEOS) and 0.17 g of polyethylene glycol (number average molecular weight: 20,000) were dissolved in a mixed solvent (weight ratio: 2/1) of N,N-dimethylimidazolidinone and propylene glycol methyl ether acetate. Then, added thereto were 0.5 g of water and 0.15 g of 0.1 N hydrochloric acid, and the resultant solution was stirred for 4 hours.

[0083] A silicon wafer having a titanium nitride thin film thereon was coated with the above solution by spin coating (revolution rate: 1,500 rpm) to thereby form a thin film. The formed thin film was heated for 1 hour at 120 °C so as to effect a gelation of the tetraalkoxysilane and remove the solvent, thereby obtaining a silica-organic polymer composite thin film.

[0084] The obtained composite thin film was calcined for 1 hour at 450 °C in an atmosphere of nitrogen gas to thereby remove the organic polymer, thereby obtaining a porous silica thin film. The obtained porous silica thin film was placed in a pressure vessel, and the internal pressure of the pressure vessel was reduced to vacuum. Then, a vapor of hexamethyldisilazane was introduced into the pressure vessel at room temperature, to thereby modify the pore surfaces with trimethylsilyl groups so as to render the pore surfaces hydrophobic. The upper surface of this thin film was coated with aluminum by vacuum deposition through a SUS mask to thereby form an electrode having a diameter of 1.7 mm. Using the thus obtained electrode-carrying porous silica thin film, the dielectric constant of the porous silica thin film was measured at 1 MHz. The dielectric constant of the porous silica thin film was found to be 3.5, which is remarkably lower than the dielectric constant (4.5) of SiO₂.

30 Examples 29 to 32

[0085] Substantially the same procedure as in Example 28 was repeated, except that the amount of polyethylene glycol was varied. The results of the dielectric constant measurement are shown in Table 5. As shown in Table 5, all of the obtained porous silica thin films exhibited low dielectric constant values.

35 Table 5

Example No.	Alkoxysilane	Polymer	Polymer/silica weight ratio	Thickness of composite film (μm)	Thickness of film after calcination (μm)	Ratio of decrease in thickness	Dielectric constant (1 MHz)
28	TEOS	PEG	0.5	0.65	0.48	26 %	3.5
29	TEOS	PEG	1.0	1.19	0.83	30 %	2.7
30	TEOS	PEG	1.5	0.93	0.63	32 %	2.5
31	TEOS	PEG	2.0	1.02	0.64	37 %	2.2
32	TEOS	PEG	3.0	1.09	0.71	35 %	1.7

50 Example 33

[0086] 0.70 g of methyltrimethoxysilane (MTMS) and 0.17 g of polyethylene glycol (number average molecular weight: 20,000) were dissolved in a mixed solvent (weight ratio: 2/1/4) of N-methylpyrrolidone, propylene glycol methyl ether acetate and methanol. Then, added thereto were 0.30 g of water and 0.15 g of 0.1 N nitric acid, and the resultant solution was stirred for 3 hours.

[0087] A silicon wafer having a titanium nitride thin film thereon was coated with the above solution by spin coating (revolution rate: 1,500 rpm) to thereby form a thin film. The formed thin film was heated for 1 hour at 120 °C so as to effect a gelation of MTMS and remove the solvent, thereby obtaining a silica-organic polymer composite thin film.

[0088] The obtained composite thin film was calcined for 1 hour at 450 °C in an atmosphere of nitrogen gas to thereby remove the organic polymer, thereby obtaining a porous silica thin film. The upper surface of this thin film was coated with aluminum by vacuum deposition through a SUS mask to thereby form an electrode having a diameter of 1.7 mm. Using the thus obtained electrode-carrying porous silica thin film, the dielectric constant of the porous silica thin film was measured at 1 MHz. The dielectric constant of the porous silica thin-film was found to be 2.8, which is lower than the dielectric constant (3.1) of $\text{CH}_3\text{SiO}_{1.5}$.

Examples 34 to 36

[0089] Substantially the same procedure as in Example 33 was repeated, except that the amount of polyethylene glycol was varied. The results of the dielectric constant measurement are shown in Table 6. As shown in Table 6, all of the obtained porous silica thin films exhibited low dielectric constant values.

Table 6

Example No.	Alkoxy silane	Polymer	Polymer/silica weight ratio	Thickness of composite film (μm)	Thickness of film after calcination (μm)	Ratio of decrease in thickness	Dielectric constant (1 MHz)
33	MTMS	PEG	0.5	1.03	0.74	28 %	2.8
34	MTMS	PEG	1.0	0.94	0.63	33 %	2.4
35	MTMS	PEG	1.5	1.06	0.67	37 %	2.1
36	MTMS	PEG	3.5	1.00	0.64	36 %	1.6

Comparative Example 9

[0090] 0.70 g of methyltrimethoxysilane (MTMS) and 0.17 g of polyethylene glycol (number average molecular weight: 20,000) were dissolved in methanol. Then, added thereto were 0.30 g of water and 0.15 g of 0.1 N nitric acid, and the resultant solution was stirred for 2 hours.

[0091] A silicon wafer was coated with the above solution by spin coating (revolution rate: 1,500 rpm) to thereby form a thin film. The formed thin film was heated for 1 hour at 120 °C so as to effect a gelation of MTMS and remove the solvent, thereby obtaining a silica-organic polymer composite thin film having a thickness of 0.87 μm.

[0092] The obtained composite thin film was calcined for 1 hour at 450 °C in an atmosphere of nitrogen gas to thereby remove the organic polymer, thereby obtaining a porous silica thin film. The thickness of the porous silica thin film was 0.45 μm, indicating that the calcination caused a thickness decrease as large as 48 %, based on the thickness of the silica-organic polymer composite thin film. It is presumed that pores which should have been formed when the organic polymer was removed by calcination were collapsed.

Comparative Examples 10 and 11

[0093] Substantially the same procedure as in Comparative Example 9 was repeated, except that the amount of polyethylene glycol was varied. The results of the measurement of the ratio of decrease in the film thickness are shown in Table 7. As shown in Table 7, the calcination caused a marked decrease in the film thickness in Comparative Examples 10 and 11.

Table 7

Compara. Ex. No.	Alkoxy silane	Polymer	Polymer/silica weight ratio	Thickness of composite film (μm)	Thickness of film after calcination (μm)	Ratio of decrease in thickness
9	MTMS	PEG	0.5	0.87	0.45	48 %
10	MTMS	PEG	1.0	0.36	0.14	61 %
11	MTMS	PEG	1.5	1.14	0.47	59 %

Example 37

[0094] 0.6 g of methyltrimethoxysilane and 0.1 g of polysebacic anhydride (number average molecular weight: 1,900) were dissolved in 1.0 g of N,N-dimethylformamide. Then, added thereto were 0.05 g of water and 0.1 g of 0.1 N hydrochloric acid, and the resultant solution was stirred for 1 hour at room temperature. This solution was cast onto a polytetrafluoroethylene watch glass to thereby form a thin film, and the formed thin film was allowed to stand for 1 hour at 100 °C to thereby cause the methyltrimethoxysilane to be gelled. Then, the thin film was dried in vacuum at 180 °C, thereby obtaining a silica-organic polymer composite thin film. The dried composite thin film was transparent.

10 INDUSTRIAL APPLICABILITY

[0095] Both of the silica-organic polymer composite thin film (which is produced by a process comprising: forming a thin film of the alkoxy silane/organic polymer composition of the present invention; subjecting the thin film to a hydrolysis and dehydration-condensation reaction with respect to the alkoxy silane thereof, to thereby cause the alkoxy silane to be gelled in the thin film; and removing the solvent remaining in the thin film by drying) and the porous silica thin film (which is obtained by removing the organic polymer from the silica-organic polymer composite thin film) have advantages not only in that these thin films have a low dielectric constant suitable for insulating layers for a multilevel interconnect for a semiconductor device, but also in that these thin films can be produced by a method which can be easily performed in the current process for producing a semiconductor device. Therefore, the alkoxy silane/organic polymer composition of the present invention for use in producing an insulating thin film can be very advantageously used for producing an insulating layer for a multilevel interconnect for a semiconductor device, such as an LSI.

Claims

25 1. An alkoxy silane/organic polymer composition for use in producing an insulating thin film, comprising:

(A) at least one alkoxy silane selected from the group consisting of (1) tetraalkoxysilanes, (2) trialkoxysilanes, (3) dialkoxy silanes, (4) monoalkoxysilanes and (5) trialkoxysilane dimers, respectively, represented by the following formulae (1), (2), (3), (4) and (5):



45 wherein each R independently represents a straight chain or branched alkyl group having 1 to 6 carbon atoms, each of R^1 , R^2 and R^3 independently represents a hydrogen atom or a nonovalent hydrocarbon group having 1 to 6 carbon atoms, and R^4 represents a divalent hydrocarbon group having 1 to 6 carbon atoms, and wherein, when said alkoxy silane (A) is at least one first alkoxy silane selected from the group consisting of said alkoxy silanes (3) and (4), said first alkoxy silane is used in combination with at least one second alkoxy silane selected from the group consisting of said alkoxy silanes (1), (2) and (5);

50 (B) at least one organic polymer having a main chain mainly comprising at least one polymer chain selected from the group consisting of an aliphatic polyether chain having ether group-containing recurring units having 2 to 12 carbon atoms, an aliphatic polyester chain having ester group-containing recurring units having 2 to 12 carbon atoms, an aliphatic polycarbonate chain having carbonate group-containing recurring units having 2 to 12 carbon atoms and an aliphatic polyanhydride chain having anhydride group-containing recurring units having 2 to 12 carbon atoms; and

55 (C) a solvent for said alkoxy silane (A) and said organic polymer (B), wherein said solvent (C) comprises at least one organic solvent selected from the group consisting of amide linkage-containing organic solvents and ester linkage-containing organic solvents.

2. The composition according to claim 1, wherein said alkoxy silane (A) is a mixture of at least one tetraalkoxysilane (1) and at least one alkoxy silane selected from the group consisting of said alkoxy silanes (2) to (5).

3. The composition according to claim 1, wherein said alkoxy silane (A) is at least one trialkoxysilane (2), or a mixture of at least one trialkoxysilane (2) and at least one alkoxy silane selected from the group consisting of said alkoxy silanes (1) and (3) to (5).

5 4. The composition according to any one of claims 1 to 3, wherein said solvent (C) further comprises at least one alcohol.

5 5. The composition according to any one of claims 1 to 4, which further comprises (D) at least one acid capable of functioning as a catalyst for promoting a hydrolysis and dehydration-condensation reaction of said alkoxy silane (A).

10 6. The composition according to any one of claims 1 to 5, wherein said organic polymer (B) is an aliphatic polyether comprising a polyalkylene glycol having C₂-C₁₂ ether group-containing recurring units and having a number average molecular weight of from 200 to 1,000,000.

15 7. The composition according to any one of claims 1 to 6, wherein said organic polymer (B) is present in an amount of from 0.1 to 10 in terms of a weight ratio relative to the amount of a product obtained by subjecting the entire amount of said alkoxy silane (A) to a hydrolysis and dehydration-condensation reaction.

20 8. A silica-organic polymer composite thin film, which is produced by a process comprising:

forming a thin film of the composition of any one of claims 1 to 7;
subjecting said thin film to a hydrolysis and dehydration-condensation reaction with respect to said alkoxy silane (A) thereof, to thereby cause said alkoxy silane (A) to be gelled in said thin film; and
removing said solvent (C) remaining in said thin film by drying.

25 9. The silica-organic polymer composite thin film according to claim 8, which has a thickness of from 0.1 to 100 µm.

10. The silica-organic polymer composite thin film according to claim 8 or 9, which is transparent to visible rays having a wavelength of from 0.4 to 0.7 µm.

30 11. A multilevel interconnect comprising a plurality of insulating layers and circuits formed on said insulating layers, wherein at least one layer of said insulating layers comprises the silica-organic polymer composite thin film of any one of claims 8 to 10.

35 12. A semiconductor device comprising the multilevel interconnect of claim 11.

13. A porous silica thin film which is obtained by removing the organic polymer from the silica-organic polymer composite thin film of any one of claims 8 to 10.

40 14. The porous silica thin film according to claim 13, which has an average pore diameter of from 1 to 500 nm.

15. The porous silica thin film according to claim 13 or 14, wherein the removal of said organic polymer from said silica-organic polymer composite thin film is performed by calcining said composite thin film at a temperature of not higher than 450 °C.

45 16. The porous silica thin film according to any one of claims 13 to 15, which has a surface thereof treated with a silylating agent.

17. A multilevel interconnect comprising a plurality of insulating layers and circuits formed on said insulating layers, wherein at least one layer of said insulating layers comprises the porous silica thin film of any one of claims 13 to 16.

50 18. A semiconductor device comprising the multilevel interconnect of claim 17.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/03186

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl' C08L83/04, 67/02, 69/00, 71/02, C08K5/10, 5/20, C08J5/18, 9/26, B32B27/00, C01B33/12, H01L21/3205, 21/316

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl' C08L83/04, 67/02, 69/00, 71/02, C08K5/10, 5/20, C08J5/18, 9/26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 8-245278, A (Director General, Agency of Industrial Science and Technology), 24 September, 1996 (24. 09. 96), Claims ; page 3, column 4, Par. No. [0013] to page 4, column 6, Par. No. [0022] (Family: none)	1-18
A	JP, 7-100389, A (Nippon Oil Co., Ltd.), 18 April, 1995 (18. 04. 95), Claims ; page 4, column 5, Par. No. [0019] to page 5, column 7, Par. No. [0027] (Family: none)	1-18

 Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search 2 October, 1998 (02. 10. 98)	Date of mailing of the international search report 13 October, 1998 (13. 10. 98)
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